

AMENDED SPECIFICATION.

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PATENT SPECIFICATION



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COMPLETE SPECIFICATION (AMENDED).

Improvements in Process of Manufacturing Esters and other Valuable Organic Compounds.

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, New Castle County, State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in processes of manufacturing esters and other valuable organic compounds.

One object of the invention is the conversion of an alcohol containing more than one carbon atom into its corresponding ester and other valuable products.

By "corresponding ester" we mean an ester formed of the alcohol converted and the fatty acid having the same number of carbon atoms as is present in the alcohol. Thus, the corresponding ester of ethyl alcohol is ethyl acetate.

Another object of the invention is the conversion of an alcohol containing more than one carbon atom into an aldehyde, an acid and an ester, in which the yield of ester predominates.

A further object of the invention is the conversion of ethyl alcohol into ethyl acetate, normal butyl alcohol and other valuable organic products.

It is well known, principally through the works of the French savant Sabatier and his collaborators, that when an alcohol vapour is passed over a dehydrogenating catalyst at atmospheric pressure and at an elevated temperature hydrogen is split off and the corresponding aldehyde is obtained. In the case of most of the alcohols the yield of aldehyde is almost quantitative.

Methyl alcohol, however, when thus

dehydrogenated, in addition to the hydrogen and aldehyde, yields some carbon monoxide from decomposition of part of the aldehyde formed, as was observed by Sabatier. It also yields appreciable amounts of methyl formate, as was first pointed out by Mannich and Geilmann, Ber. 49,585—6 (1916), presumably from condensation of the aldehyde.

With the exception of U.S. Patent to Herman F. Wilkie, No. 1,400,195, entitled "Process of Making Methyl Formate", and U.S. Patent to David A. Legg and Charles Bogin, No. 1,580,143, entitled "Production of Esters", the literature records no instance where alcohols other than methyl alcohol yields esters in any considerable amount. The U.S. Patent to Herman F. Wilkie, No. 1,400,195 confirms the observation of Mannich & Geilmann. The U.S. Patent to David A. Legg, et al, No. 1,580,143 covers the conversion of butyl alcohol to butyl butyrate. According to each of these references, these processes are operated at atmospheric pressure.

From a consideration of known laws of physical chemistry, increasing the pressure would be expected to decrease the amount of reaction per passage for the dehydrogenation is accompanied by an increase in volume. This fact would indicate that an attempt at dehydrogenation by increase of pressure would be useless.

We have discovered, however, that if the dehydrogenation of primary alcohols other than methyl alcohol is carried out under pressure the character of the products obtained undergoes a marked change. Instead of obtaining only aldehyde and hydrogen, with at best only

small amounts of accompanying ester, the dehydrogenation when conducted under pressure yields the corresponding ester as the principal product, while the corresponding alcohol of twice the number of carbon atoms is formed in considerable amount and the corresponding aldehyde and acid are formed in much less amounts. Other products, for example, unsaturated alcohols and esters corresponding to higher alcohols, may be formed. For example, when using ethyl alcohol as a starting material, the vapour phase dehydrogenation at atmospheric pressure in the presence of copper will give a conversion of 50 per cent of the alcohol per passage, the remaining 50 per cent passing through unchanged. Of the alcohol converted 11 per cent will be converted to the ester, the remainder going to acetaldehyde. When operating under a pressure of 270 atmospheres, for example, 50 per cent of the alcohol is again converted per passage, 5 per cent or slightly more is broken down into carbon monoxide and methane and 45 per cent or so comes through unchanged. Of the alcohol converted about half goes to ethyl acetate, about a fourth goes to normal butyl alcohol and the remaining fourth appears as acetic acid and acetaldehyde. All of these products are useful in the arts and more valuable than the ethyl alcohol from which they are made.

In the following embodiment of the invention we show by an example, a mode of applying these principles in the production of ethyl acetate. It will be obvious, however, that many modifications in the conditions under which this process can be carried out may be made. Thus, for instance we find a temperature of from 250 to 500° C. and a pressure of more than ten atmospheres to be desirable for carrying out this process.

Ethyl alcohol is pumped into a boiling vessel maintained at a temperature above the critical temperature of the alcohol, e.g. 300° C., where it is converted to vapour under pressure. This vapour is then conducted to a pressure-resisting tube in which the catalyst is contained. The catalyst consists of copper oxide to which a few percent each of manganese oxide and magnesium oxide have been added, reduced carefully before use and maintained at a temperature of 350° C. The vapour is passed through this catalyst at a rate equal to four volumes of liquid ethyl alcohol for each volume of the catalyst per hour.

The effluent gases are passed under pressure through a condensing coil, when

there separates unchanged ethyl alcohol containing in solution about 18 percent by weight of ethyl acetate, 12 percent of normal butanol, 3 percent of acetic acid and 3 percent of acetaldehyde, with smaller amounts of higher boiling oxygenated organic compounds. The uncondensed hydrogen is bled out of the system at such a rate as to maintain the pressure in the system at 275 atmospheres. This hydrogen is, of course, a valuable by-product, as it is of good purity.

The conditions under which the process is carried out can be widely varied without departing from the spirit of the invention. The pressure and temperature may be varied within certain limits. Increased pressure permits the employment of higher operating temperatures without encountering undesired side reactions, thus increasing the productivity of the catalyst. This, in turn, increases the relative amount of the higher alcohol formed. The absolute amount of ester is also increased by increase in temperature, provided this increase is not pushed to the point where decomposition to carbon monoxide, methane and carbon dioxide becomes excessive. This point lies higher the higher the pressure. There is thus an intimate relation between temperature and pressure, differing with the activity of the catalyst, but easily ascertainable by trial, which permits of considerable flexibility in the composition of the product obtained.

It is of course obvious to one skilled in the art that a mixture of alcohols may be employed, in which case mixed esters are obtained, whose relative preponderance depends upon the proportions of the starting material and conditions selected for the reaction.

An incidental advantage of the process in carrying it into production on the large scale has to do with the thermal effect. Dehydrogenations at atmospheric pressure are strongly endothermic and consequently supplying the necessary amount of heat to the catalyst to maintain the reaction temperature presents a serious problem on the large scale. When conducting the operation under pressure, however, the reaction is much less endothermic and may even become slightly exothermic, thus ameliorating or entirely removing the problem of heat supply.

Catalysts which are suitable for this process are all those catalytic materials which are classed as dehydrogenating agents. Metals such as copper, nickel, cobalt and iron, either alone or in admixture, or with the addition of oxides of

other metals, such as manganese oxide, chromium oxide, magnesium oxide or calcium oxide, have proved satisfactory, or oxide catalysts which are known to dehydrogenate alcohols can be used, either singly or in combination. These comprise such materials as zinc oxide, magnesium oxide, chromium oxide, manganese oxide and so on.

10 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

15 1. An improved process of converting a primary alcohol or a mixture of primary alcohols containing more than one carbon atom into its corresponding ester or esters and other organic products, by
20 vaporising the alcohol or mixture of alcohols and conducting it over a dehydrogenating catalyst at an elevated temperature, characterised in this that the catalysis is carried out at an elevated
25 pressure.

2. An improved process of converting a primary alcohol containing more than one carbon atom into its corresponding ester and other organic products, as
30 claimed in Claim 1, characterised in this that ethyl alcohol is used whereby products including the following compounds are obtained: ethyl acetate, normal butyl alcohol, and acetaldehyde.

3. An improved process of catalytically dehydrogenating ethyl alcohol as claimed in Claim 3, characterised in this that ethyl alcohol in vapour phase is passed over a catalyst at a temperature of from 250° to 500° C. at a pressure higher than
40 10 atmospheres.

4. An improved process of dehydrogenating primary alcohols to form the corresponding esters and other organic compounds as claimed in Claims 1 to 3, which comprises vaporizing the alcohol and conducting the vapour over a dehydrogenating catalyst at a pressure above normal, and at a temperature somewhat below the point at which for the pressure employed, excessive decomposition occurs within formation of oxides of carbon.
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5. The improved process of converting a primary alcohol or mixture of primary alcohols into the corresponding ester or esters and other organic products, substantially as hereinbefore described.
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6. Organic compounds whenever prepared or produced by the improved processes hereinbefore described and claimed.
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Dated this 12th day of March, 1928.

MARKS & CLERE.

Reference has been directed, in pursuance of Section 8, Sub-Section 2, of the Patents and Designs Acts, 1907 to 1928, to Specification No. 282,448.